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**ESTIMATION OF THE THERMOPHYSICAL AND MECHANICAL
PROPERTIES AND THE EQUATION OF STATE OF Li_2O**

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ESTIMATION OF THE THERMOPHYSICAL AND MECHANICAL PROPERTIES AND THE EQUATION OF STATE OF Li_2O *

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ABSTRACT. In this study we develop correlation methods based on Knoop micro-hardness and melting points for estimating tensile strength, Young's modulus, and Poisson's ratio for Li_2O as a function of grain size, porosity, and temperature. We develop generalized expressions for extrapolating the existing data on thermal conductivity and thermal expansivity. These derived thermophysical data are combined to predict thermal stress factors for Li_2O . Based on the available vapor pressure data on Li_2O and empirical correlations for the liquid and vapor equation of state of Li_2O , we also make estimates of the critical properties of Li_2O and obtain a critical temperature of approximately 6800 ± 800 K.

1 INTRODUCTION

Lithium oxide is potentially the best solid breeder material for use in magnetic or inertial-confinement fusion reactors because of its uniquely high lithium atom density coupled with a high melting point and relatively low volatility. The lithium atom density in Li_2O ($\sim 0.88 \text{ MgLi/m}^3$ at 1000 K) exceeds that in the pure metal by a factor of 2 and that in $\gamma\text{-LiAlO}_2$, the leading contender as a solid breeder, by a factor of 3. This high lithium atom density permits Li_2O to achieve a tritium breeding ratio of greater than one in a fusion reactor blanket without the use of neutron multipliers as required with other solid breeders.

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In development of Li_2O as a solid breeder material, there is much yet to be done in establishing its fabrication characteristics, its compatibility with other materials, and its thermophysical and mechanical properties for design purposes. It has been only recently that the thermal expansivity was measured by Kurasawa and coworkers (1982), the thermal conductivity was measured by Takahashi and Kikuchi (1980), and an accurate value for the melting point was determined by Ortman and Larsen (1982). Considerable work has been done on the vaporization characteristics of Li_2O , and these studies have been summarized by Lamoreaux and Hildenbrand (1984). The microhardness of Li_2O has been reported by Nasu and coworkers (1978). We make estimates in this paper of some of the unknown properties using mainly correlation methods. In addition to estimating properties of the solid we will also estimate the liquid-gas coexistence curve and the critical properties of Li_2O as a basis for better understanding its behavior in the liquid state.

2 ESTIMATION OF THE THERMOPHYSICAL AND MECHANICAL PROPERTIES OF Li_2O

Thermal Conductivity

Takahashi and Kikuchi (1980) measured thermal diffusivities of Li_2O in the range of 70.8 to 93.4% of theoretical density (TD) and derived thermal conductivities using available specific heat and density data. We slightly modify their expression for thermal conductivity k to put it in terms of volume fraction porosity p instead of fraction of TD as follows:

$$k = (1 - p)^{1.94} (0.0220 + 1.784 \times 10^{-4} T)^{-1}, \text{ W/m-K.} \quad (1)$$

Thermal Expansivity

Kurasawa and coworkers (1982) measured the thermal expansion up to ~1200 K for two single crystal specimens and five sintered specimens of Li_2O using dilatometry. Agreement appears to be good for percent thermal expansion from room temperature up to about 1100 K for the various specimens. Above 1100 K,

however, the percent expansion curve show variations between the different single crystal runs, and a drop-off in slope with increasing temperature for sintered samples with 80.0, 86.7, and 91.1% of TD, but a normal continuation of the curves for 75.5, 92.5, and 100.0% of TD.

Our approach is to fit an average curve to the fractional expansion data up to 1100 K, and then allow the curve to rise in a predicted way above that temperature. The functional form of the curve is taken to be one that has previously been shown by Krikorian (1971) to be applicable to a large number of substances, including metals, oxides, borides, carbides, and nitrides, particularly at high temperatures. Thus, the averaged expressions for fractional linear expansion, $\Delta L/L_0$ (where L_0 is referred to 298 K), and linear thermal expansivity, α , are:

$$\Delta L/L_0 = -4.275 \times 10^{-3} + 1.4692 \times 10^{-6} T^{1.4}, \quad (2)$$

$$\alpha = d(\Delta L/L_0)/dT = 2.0569 \times 10^{-6} T^{0.4}, K^{-1}. \quad (3)$$

Mechanical Properties

Because of the lack of mechanical property data on Li_2O , we will rely on correlations based on other oxides to obtain some rough values. A primary design need for mechanical properties for Li_2O is to evaluate the thermal stress parameter, M , defined as follows:

$$M = \frac{\sigma_t (1 - \nu)k}{E\alpha}, \quad (4)$$

where σ_t is the short term tensile strength, ν is Poisson's ratio, k is thermal conductivity, E is Young's modulus, and α is the linear thermal expansivity.

We consider first the estimation of tensile strength for Li_2O . We will attempt to correlate the tensile of Li_2O with the microhardness which has recently been measured by Nasu and coworkers (1978). Their as-prepared

sintered specimens (grain size $\sim 50 \mu\text{m}$) gave a Vickers microhardness of $180 \pm 8 \text{ kg/mm}^2$ using a 300 g load for 30s on a diamond indenter.

In order to develop a correlation between microhardness and tensile strength, we need data on oxides that have been adequately characterized for grain size and porosity. Recognizing the difficulties in obtaining reliable tensile strengths for ceramics, we nonetheless use data on microhardness and tensile strength given by Samsonov (1973) and Shaffer (1964) to obtain a rough correlation (see Fig. 1). Knoop rather than Vickers microhardness is used since that is what is generally available. Grain sizes for the oxides are about $30 \mu\text{m}$, porosities about 3%, and tensile strengths refer to ultimate short-term tensile strengths. From Fig. 1, we predict a tensile strength of about 20.5 MPa for Li_2O having a $30 \mu\text{m}$ grain size and 3% porosity.

The variation of strengths of ceramics with grain size and porosity is expressed in a generalized form by the following empirical expression originally given by Knudsen and referenced by Conrad (1970) and Wachtman (1967):

$$\sigma = \sigma_0 d^{-n} \exp(-bp), \quad (5)$$

where σ is the strength, d is grain diameter, p is the volume fraction porosity, and σ_0 , n , and b are empirical constants. The general form of this equation differs slightly from that obtained from theoretical approaches, but the empirical expression seems to correlate well with oxide ceramics that have been studied. The value of n is usually somewhat less than 0.5, and b is about 10 according to Conrad (1970) and Wachtman (1967). Thus, using the value of 20.5 MPa for the tensile strength of Li_2O at a grain size of $30 \mu\text{m}$ and a porosity of 3%, we obtain:

$$\sigma_t(\text{Li}_2\text{O}) = 108 d^{-0.4} \exp(-10p), \text{ MPa}, \quad (6)$$

where d is expressed in μm .

In line with the behavior of other ceramics we expect that the strength of Li_2O will not vary significantly with temperature up to about 55-60% of its melting temperature at which point the strength will begin to decrease. This behavior can be expressed approximately by the relationship

$$\sigma_t = \sigma_o (1 - 44 \exp(-7000/T)). \quad (7)$$

We discuss next the estimation of Young's modulus for Li_2O . From discussions of the theories on ceramics by Wachtman (1967) and Conrad (1970) and data presented by Shaffer (1964) and Samsonov (1973), we conclude the following. We can make a rough estimate of Young's modulus for Li_2O by correlating values of Young's modulus with the melting point of oxides. Grain size has no significant effect on Young's modulus at temperatures below the onset of grain-boundary sliding (i.e., below ~0.55-0.60 of the absolute melting point). However, porosity has a major effect on the modulus, leading to a decrease in modulus with increasing porosity. The effect of temperature is to give a slow rate of decrease of Young's modulus with increasing temperature until grain-boundary sliding sets in, at which point the modulus decreases rapidly until the melting point is reached. Elastic constants are very dependent on structure, so that the various generalized conclusions discussed above only apply if phase transitions do not occur over the temperature interval of interest. Li_2O meets this criterion.

We apply the correlation of Young's modulus versus melting point to only the cubic oxides (Li_2O has a cubic inverse fluorite structure), and use the available data from Shaffer (1964) and Samsonov (1973) after extrapolating to zero porosity. The cubic oxide correlation is illustrated in Fig. 2, where data on several representative cubic metals obtained from Samsonov (1968) are also included to show that the generalized correlation between Young's modulus and melting point is expected to be approximately linear. Data on non-cubic

oxides such as Al_2O_3 and BeO show a significant deviation from the correlation, thus emphasizing structural effects. For Li_2O with a melting point of 1711 K (Ortman and Larson, 1982), we predict from Fig. 2 a Young's modulus of about 140 GPa at room temperature and zero porosity.

To predict the variation of Young's modulus with the porosity of Li_2O , we use the empirical Spriggs expression given by Conrad (1970) and Wachtman (1967):

$$E = E_0 \exp(-bp), \quad (8)$$

where E_0 is the value of Young's modulus at zero porosity (i.e., 140 GPa), b is an empirical constant, and p is the fractional porosity. We find b values of 4.0 for Al_2O_3 , 4.7 for MgO , and 3.4 for BeO from data given by Samsonov (1973), Shaffer (1964), Conrad (1970) and Wachtman (1967). We therefore take $b = 4.0$ for Li_2O as our best guess, and the Spriggs expression for Li_2O becomes:

$$E(\text{Li}_2\text{O}) = 140 \exp(-4.0 p), \text{ GPa}. \quad (9)$$

According to Wachtman (1967), the temperature dependence of Young's modulus for ceramics can be described by an empirical expression of the type:

$$E = E_0 - AT \exp(-B/T), \quad (10)$$

where E_0 is Young's modulus at absolute zero, and A and B are empirical constants for each material. We find that we can put equation (10) into a more generalized form by assuming (1) that E goes to zero at the melting point, and (2) that the constant B is equal to the melting temperature. The expression thus becomes

$$E = E_0 - (T/T_m) E_0 \exp(1 - T/T_m), \quad (11)$$

where T_m is the melting point. Examining the available data for Al_2O_3 , MgO , ThO_2 , UO_2 , and MgO and CaO stabilized ZrO_2 as given by Samsonov (1973) and Shaffer (1964), we find that there is good agreement with this expression up to at

least 1200 K, and in some cases up to 1800 K (see Table 1). Predicted values for Li_2O with zero porosity are also summarized in Table 1.

It is difficult to make an accurate estimate of Poisson's ratio for Li_2O . Wide variations are seen in the reported data for even conventional ceramic materials such as Al_2O_3 and MgO (see Fig. 3) as based on data given by Samsonov (1973), Shaffer (1964), and Soga and Anderson (1966). We therefore choose to take roughly a mean value, based on all materials, of $\nu = 0.25$ for Li_2O , and further assume that ν is independent of porosity, temperature, and chemical purity.

Thermal Stress Parameter

We are now in a position to calculate values of the thermal stress parameter M for Li_2O as defined in equation (4). Analytical expressions are summarized in Table 2 for each of the input parameters, together with estimates of the uncertainties. It is evident from Table 2 that the uncertainties in the mechanical properties (σ_t , E , and ν) are quite large and translate into an overall uncertainty of about an order of magnitude in the thermal stress parameter M .

Even though the absolute value of the thermal stress parameter is not very accurate, it is still useful for us for design purposes to know the dependence of M on grain size, porosity, and temperature in attempting to optimize use conditions for Li_2O in a fusion reactor blanket. Thus the porosity and temperature dependence of M for Li_2O with a grain diameter of 10 μm are illustrated in Fig. 4.

3 ESTIMATION OF LIQUID-GAS COEXISTENCE CURVE AND CRITICAL PROPERTIES OF

Li_2O

The Gas Phase Composition Above Liquid Li_2O

In analyzing the gas phase composition above liquid Li_2O , we assume that Li_2O is vaporizing under relatively neutral conditions, and is undergoing con-

gruent vaporization. We refer to both the recent thermodynamic data compilation of Lamoreaux and Hildenbrand (1984) up to 3000 K, and the JANAF (1971) data up to 6000 K, to summarize in Table 3 the relative moles of gaseous species produced for each mole of liquid Li_2O vaporized at temperatures of 2000-6000 K. Also, summing over the various partial pressures, we obtain the total gas pressure at saturation, P_{sat} , in the last column of Table 3, by assuming ideal gas behavior.

We now approximate the temperature dependence of P_{sat} by using an equation having the form of the Clapeyron equation, i.e.,

$$\ln P_{\text{sat}} = A + B/T, \quad (12)$$

and find that if we plot $\log P_{\text{sat}}$ versus $1/T$ for the data given in Table 3, we obtain a good fit given by

$$\ln P_{\text{sat}} (\text{Pa}) = 24.83 - 36,300/T. \quad (13)$$

Estimation of Liquid and Vapor Densities

As a first step in establishing liquid and vapor densities for the liquid-gas coexistence curve of Li_2O , we need to estimate the density of liquid Li_2O at its melting point of 1711 K. Using the room temperature lattice constant for Li_2O ($a_0 = 0.4619 \text{ nm}$) given by Wyckoff (1963) and taking the volume expansion to be 3 times the linear expansion given by equation (2), we obtain a molar volume of $16.85 \text{ cm}^3/\text{mole}$ for the solid at the melting point, which gives a density of $\rho = 1.773 \text{ Mg/m}^3$.

In order to estimate the density of the liquid, we now examine the available information on volume change upon fusion of compounds with the fluorite structure as well as the alkali halides and various oxides (see Table 4). Thus, we see that the very approximate value of +15.4% that is available for the volume change upon fusion of Li_2O is higher than observed for other com-

pounds with the fluorite structure. Yet, this may not be unreasonable, since upon examining the data on alkali halides, we find that the lithium halides show a higher $\Delta V_f/V_g$ value than the other alkali halides. The value for Li_2O also falls well within the observed range of values for oxides. We therefore take $\Delta V_f/V_g$ for Li_2O to be $15.4 \pm 5\%$ and calculate $\Delta V_f = 2.60 \text{ cm}^3/\text{mole}$, or $V_l = 19.45 \text{ cm}^3/\text{mole}$ and $\rho_l = 1.536 \text{ Mg/m}^3$ for liquid Li_2O at its melting point.

We now proceed to estimate the change of density of liquid Li_2O with temperature. We first apply a corresponding states expression for liquid density of liquid Li_2O developed by Riedel and reported by Lewis and coworkers (1961) as

$$\rho_l/\rho_c = 1 + 0.85(1 - T_r) + (1 - T_r)^{1/3}(1.89 + 0.91/\omega), \quad (14)$$

where ρ_l and ρ_c are the liquid and critical densities, T_r is the reduced temperature, and ω is the acentric factor used by Riedel as a measure of the departure of the intermolecular potential function from that of simple spherical molecules. If we let $T_r = 0$ in equation (14), as indicated by Riedel, we obtain a hypothetical density ratio at absolute zero of $\rho_0/\rho_c = 3.74 + 0.91 \omega$. Dividing this into equation (14), we find that the resultant expression is insensitive to ω up to about $T_r = 0.8$, and the expression takes the form

$$\rho_l/\rho_0 = 0.2674 + 0.2273(1 - T_r) + 0.505(1 - T_r)^{1/3}. \quad (15)$$

Now, anticipating that T_c will be somewhere in the vicinity of 7000 K, we find from equation (15) that $\rho_l/\rho_0 = 0.8991$ at 1711 K, and from our reference density value of 1.536 Mg/m^3 at 1711 K, we obtain $\rho_0 = 1.708 \text{ Mg/m}^3$, which gives

$$\rho_l = 0.4568 + 0.3883(1 - T_r) + 0.863(1 - T_r)^{1/3}, \text{ Mg/m}^3. \quad (16)$$

Values of liquid density calculated from this expression up to ~ 0.8 of T_c are shown in Fig. 5. We note also that using values of T_c of 6500 K or 7500 K in equation (16) does not significantly change the calculated values of ρ_l plotted in Fig. 5.

We now take as an alternative approach for estimating ρ_h , the hole theory for liquids as developed by Fürth (1941), and applied with good results by Bockris and Richards (1957) to the liquid alkali halides. Hole theory assumes that a fraction θ of the liquid has essentially the same structure as the corresponding solid, and within the volume of this solid-like structure are holes with a characteristic size which depends upon the surface tension of the fluid. The characteristic hole size, v_h , is given by Fürth as

$$v_h = (32/15\pi)(kT/\sigma)^{3/2}, \quad (17)$$

where k is the Boltzman constant and σ is the surface tension of the liquid. In order to calculate θ , Fürth compares the characteristic hole size with the size of a particle in the solid lattice and obtains solutions for three cases, namely: for hole sizes comparable to particle size $\theta = 0.37$, and for hole sizes either much smaller or much larger than the particle size $\theta = 0.915$. Once θ is established, we can calculate the volume thermal expansivity, β , for the liquid using the relation

$$\beta = \beta_s \theta + \beta^*, \quad (18)$$

where β_s is the volume thermal expansivity of the solid extrapolated into the liquid region, and β^* is the contribution to the volume thermal expansivity by the holes. By assuming that the surface tension has the characteristic form

$$\sigma = a(1 - T_r)^b, \quad (19)$$

where a and b are parametric constants, and that the holes are single holes only (rather than associated), Fürth obtains the following expression for β^* ,

$$\beta^* = \frac{v_h N_h}{V_l} \frac{(3/2)[T_c + T(b - 1)]}{T(T_c - T)}, \quad (20)$$

where N_h is the number of holes per mole, and b , according to Lewis and coworkers (1961), has the value 11/9. The factor $v_h N_h/V_l$ is most conveniently

estimated from the volume change on fusion, i.e., $\Delta V_f/V_s$, which in our case is $2.60/19.45 = 0.1337$. The extrapolated volume thermal expansivity of the solid, β_s , taken as 3 times the linear thermal expansivity from equation (3), is

$$\beta_s = 6.171 \times 10^{-6} T^{0.4}. \quad (21)$$

Before proceeding with the hole theory calculation, we need to compare hole size, v_h , with the lattice particle size in Li_2O . To do this, we need an estimate of the surface tension of liquid Li_2O . Using a modified form of the Eötvös equation, we will assume for a given class of compounds that $\sigma V_a^{2/3}$ is proportional to enthalpy of vaporization at the boiling point, ΔH_v , where V_a is the volume per gram-atom and ΔH_v is also given on a gram-atom basis. Thus, comparing the available data on oxides (see Table 5), we find that the product $\sigma V_a^{2/3} \Delta H_v^{-1}$ remains reasonably constant with an average value of 5.72×10^{-7} Newton-m/kJ at a temperature of $\sim 2/3$ of the boiling point. We therefore estimate the surface tension of liquid Li_2O to be 3.28 Newtons/m at 1711 K (see Table 5).

Using this surface tension value in equation (17), we obtain a characteristic hole volume of $1.3 \times 10^{-23} \text{ cm}^3$ at the melting point of Li_2O . This can be compared with the size of the O^{2-} ion, which, assuming an ionic radius of $\sim 0.14 \text{ nm}$, is $1.15 \times 10^{-23} \text{ cm}^3$ at room temperature. The volume of Li^+ is about an order of magnitude smaller than this, and an Li_2O unit occupies on the average a volume of $3.2 \times 10^{-23} \text{ cm}^3$ based on the density of solid Li_2O . We will assume that it is the size of the O^{2-} ion that mainly defines the particle size for purposes of the hole theory, and since v_h is therefore comparable in size to O^{2-} , and we will take Fürth's value of 0.37 for θ .

Substituting equations (20 and (21) into equation (18) together with $v_h N_h/V_s = 0.1337$, $T_c = 7000 \text{ K}$, $b = 11/9$, and $\theta = 0.37$, and then integrating equation (18), we obtain

$$V_L (\text{Li}_2\text{O}) = 19.45 \exp [0.8582 + 1.631 \times 10^{-6} T^{1.4} + 0.300 \ln T - 0.367 \ln (7000 - T)], \text{ cm}^3/\text{mole}. \quad (22)$$

We also note that substituting either $T_c = 6000 \text{ K}$ or 8000 K in equation (22) has little effect on the values of V_L up to ~ 0.8 of T_c .

Using equation (22), we now calculate the values of ρ_L for Li_2O based on hole theory as shown by the full triangles in Fig. 5. We see that the rate of density decrease with temperature is substantially greater based on hole theory than based on the Riedel equation. We believe that the hole theory densities are actually too low because of the assumption of a regular rate of decrease of σ with temperature (see equation (19)). Many liquid oxides such as B_2O_3 , SiO_2 , GeO_2 , PbO , and LiBO_2 (see Janz and coworkers, 1969) show an increase in σ with temperature (even though this trend must reverse as the critical point is approached). We believe the Riedel equation densities are too high, because the rate of decrease of density with temperature is less than that in solid Li_2O . We conclude that the true values of ρ_L lie somewhere between the hole theory and Riedel equation values.

We next proceed to sketch in the rectilinear diameters, D_R , based on both the hole theory and Riedel equation ρ_L values, where D_R is given by

$$D_R = (\rho_L + \rho_g)/2, \quad (23)$$

and ρ_g is the density of the gas, which for our purposes here is taken to be the ideal gas density derived from equation (13) by using an average molecular weight for the gas phase. We further sketch in a locus of critical densities by assuming a series of critical temperatures and correcting the ideal gas densities to that of a real gas at each assumed critical point using a critical compressibility factor of 0.291 as listed by Lewis and coworkers (1961) for an accentric factor of zero. Using Riedel's method of vapor pressures for calculating the accentric factor, we find that the accentric factor actually is \sim

zero. We thus find (see Fig. 5) that the hole theory rectilinear diameter gives $T_c = 6400$ K, and the Riedel equation rectilinear diameter gives $T_c = 7350$ K. We select 6800 ± 800 K as our best estimate of T_c , and construct the coexistence curve as shown by the solid line in Fig. 5 to give a linear variation of rectilinear diameter with temperature. The real gas densities used in constructing Fig. 5 are summarized in Table 6.

Summarizing the estimated critical properties of Li_2O from Table 6, we find a critical temperature of 6800 ± 800 K, a critical pressure of $\sim 2.9 \times 10^8$ Pa, a critical density of ~ 0.32 Mg/m³, and a critical volume of ~ 93 cm³/mole.

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Figure 1. A correlation of Knoop microhardness with tensile strength is illustrated for several oxide ceramics having an approximate grain size of 30 μm and a porosity of about 3%.

Figure 2. The correlation of Young's modulus of elasticity with melting point is illustrated here for cubic oxides and metals.

Figure 3. Poisson's ratio is shown as a function of temperature for several oxides. The solid curves are from Samsonov (1973) and the dashed curves from Soga and Anderson (1966).

Figure 4. Illustrated here are calculated values of the thermal stress factor M for Li_2O as a function of temperature and porosity at a fixed grain diameter size of 10 μm .

Figure 5. Predicted coexistence curve for Li_2O liquid and gas.

Table 1. The observed variation of Young's modulus (in GPa) with increasing temperature is compared for several oxide ceramics with the behavior calculated using equation (11). Predicted values for Li_2O are given in the last column.

T, K	Al_2O_3		MgO		$\text{ZrO}_2 - 4\% \text{ CaO}$		ThO_2		Li_2O
	(p = 2%)		(p = 2%)		(p = 4%)		(p = 3%)		(p = 0%)
	obs.	calc.	obs.	calc.	obs.	calc.	obs.	calc.	calc.
298	376	376	295	295	167	167	235	235	140
600	366	370	278	294	164	166	231	235	134
1000	344	333	257	279	155	159	216	229	108
1400	294	258	234	244	122	142	200	214	63

Table 2. Analytical expressions are summarized for the estimated thermo-physical and mechanical properties of Li_2O and the expected uncertainties.

Tensile strength (in MPa):

$$\sigma_t = 108 d^{-0.4} \exp(-10p) (1 - 44 \exp(-7000/T)),$$

where d = grain diameter in μm and p = volume fraction porosity.
Estimated uncertainty in σ_t is a factor of 2 to 3.

Young's modulus (in GPa):

$$E = 140 \exp(-4p) - 140(T/T_m) \exp(-4p) \exp(1 - T_m/T),$$

where T_m is the melting point of Li_2O (1711 K).
Estimated uncertainty in E is a factor of 2 to 3.

Poisson's ratio:

$$\nu = 0.25$$

Estimated uncertainty in ν is a factor of 2.

Thermal conductivity (in W/m-K):

$$k = (1 - p)^{1.94} (0.0220 + 1.784 \times 10^{-4} T)^{-1}$$

Estimated uncertainty in k is about $\pm 5\%$.

Linear thermal expansivity (in K^{-1}):

$$\alpha = 2.0569 \times 10^{-6} T^{0.4}$$

Estimated uncertainty in α is about $\pm 7\%$.

Table 3. Listed here are the estimated equilibrium concentrations of gaseous species above congruently vaporizing liquid Li_2O . The total saturation gas pressure above liquid Li_2O based on these species is given in the last column.

T, K	$P_{\text{Li}_2\text{O}}, \text{ Pa}$	Moles of gaseous species produced for each mole of $\text{Li}_2\text{O}(l)$ vaporized ^a								$P_{\text{sat}}, \text{ Pa}$
		$\text{Li}_2\text{O}(g)$	$\text{Li}(g)$	$\text{O}_2(g)$	$\text{LiO}(g)$	$\text{Li}_3\text{O}(g)$	$\text{Li}_2\text{O}_2(g)$	$\text{O}(g)$	$\text{Li}_2(g)$	
2000	5.5×10^2	0.828	0.278	0.060	0.030	0.008	0.006	0.002	--	8.0×10^2
2500	1.8×10^4	0.754	0.334	0.064	0.074	0.024	0.006	0.008	--	3.0×10^4
3000	1.7×10^5	0.646	0.414	0.070	0.132	0.050	0.006	0.020	--	3.5×10^5
3500	8.0×10^5	0.544	0.494	0.068	0.204	0.066	0.006	0.038	0.002	1.8×10^6
4000	2.1×10^6	0.464	0.530	0.056	0.282	0.080	0.006	0.050	0.004	6.8×10^6
5000	9.4×10^6	0.348	0.624	0.050	0.344	0.100	0.004	0.100	0.014	4.2×10^7
6000	2.4×10^7	0.298	0.612	0.046	0.366	0.110	0.002	0.116	0.028	1.3×10^8

^a In addition to the neutral species listed at 6000 K, the gas also contains the following numbers of moles of charged species: $0.010 \text{ Li}^+(g)$, $0.006 \text{ Li}_3\text{O}^+(g)$, $0.008 \text{ LiO}^-(g)$, and $0.008 \text{ e}^-(g)$.

Table 4. Summary of values of the volume change on fusion relative to the volume of the solid at the melting point, $\Delta V_f/V_s$ (in %), for various halides and oxides.^a

<u>Fluorite structures</u>		<u>Alkali halides</u>		<u>Oxides</u>	
Li ₂ O	~15.4 ^b	LiF	29.4	PbO	15.6
CaF ₂	9.5	LiCl	26.2	B ₂ O ₃	9.0
SrF ₂	7.6	LiBr	24.3	Al ₂ O ₃	22.3
BaF ₂	5.8	ave., all MX:	20.0	SiO ₂	-7.6
SrCl ₂	1.9	range, all MX: 10.0-29.4			
BaCl ₂	-0.2				
UO ₂	10.4				

^a Liquid density data for the various halides, Li₂O, PbO, and B₂O₃ are from Janz (1967) and Janz and coworkers (1968), for UO₂ from Fink and coworkers (1981), for Al₂O₃ from Kirshenbaum and Cahill (1960), and for SiO₂ the data are those on SiO₂ glass given by Touloukian and coworkers (1977) with our extrapolation to the melting point. The solid density data for UO₂ are from Fink and coworkers (1981), for PbO and B₂O₃ are estimated, for SiO₂ from Skinner (1966), for Li₂O from equation (2), and the balance are from Touloukian and coworkers (1977) and Janz (1967) with extrapolations as needed.

^b This value for the volume change on fusion of Li₂O is based on an estimated molar volume derived from data on silicate melts at 1673 K (Janz, 1967). The stated uncertainty of the estimate gives the range of $\Delta V_f/V_s$ values to be from 0.6-30.2%.

Table 5. This table illustrates the constancy of the surface tension parameter, $\sigma V_a^{2/3} \Delta H_v^{-1}$, for liquid oxides at $\sim 2/3$ of the boiling point.^a

Liquid oxide	T, K	σ , Newtons/m	V_a , cm ³ /g-atom	ΔH_v , kJ/g-atom	Est. B.P., K	$\sigma V_a^{2/3} \Delta H_v^{-1}$, 10 ⁷ x Newton-m/kJ
PbO	1223	1.334	13.89	131.4	1808	5.87
B ₂ O ₃	1673	0.971	9.36	72.3	2338	5.96
Al ₂ O ₃	2323	6.95	6.77	437.8	3800	5.68
SiO ₂	2073	3.075	9.07	249.1	2800	5.37
Li ₂ O	1711	3.28 (calc.)	6.48	199.4	2730	5.72 (ave.)

^a Data for σ are from Janz and coworkers (1969). Data for V_a are from Janz (1967) for PbO, from Janz and coworkers (1968) for B₂O₃, from Kirshenbaum and Cahill (1960) for Al₂O₃, from Touloukian and coworkers (1977) for SiO₂ as based on SiO₂ glass plus extrapolated data, and for Li₂O from this report. Data for ΔH_v have been derived from JANAF (1971) using the estimated boiling points given in this table.

Table 6. Summarized here for $T_c = 6800$ K for Li_2O are values of P_{sat} , average molecular weight, ideal gas density, and real gas density based on z factors listed by Lewis and coworkers (1961).

T, K	P_{sat} , Pa	ave. MW	ρ_g (ideal), Mg/m ³	z	ρ_g (real), Mg/m ³
2000	7.93×10^2	24.86	1.19×10^{-6}	0.990	1.20×10^{-6}
2500	2.99×10^4	23.64	3.40×10^{-5}	0.985	3.45×10^{-5}
3000	3.36×10^5	22.33	3.01×10^{-4}	0.975	3.09×10^{-4}
3500	1.89×10^6	21.01	1.37×10^{-3}	0.968	1.41×10^{-3}
4000	6.93×10^6	20.30	4.23×10^{-3}	0.951	4.45×10^{-3}
4500	1.89×10^7	19.53	9.91×10^{-3}	0.921	1.08×10^{-2}
5000	4.25×10^7	18.86	1.93×10^{-2}	0.868	2.25×10^{-2}
5500	8.23×10^7	18.68	3.36×10^{-2}	0.794	4.23×10^{-2}
6000	1.43×10^8	18.56	5.31×10^{-2}	0.696	7.63×10^{-2}
6500	2.27×10^8	18.39	7.73×10^{-2}	0.551	1.40×10^{-1}
6600	2.47×10^8	18.33	8.26×10^{-2}	0.508	1.63×10^{-1}
6700	2.68×10^8	18.27	8.81×10^{-2}	0.450	1.96×10^{-1}
6800	2.91×10^8	18.21	9.36×10^{-2}	0.291	3.22×10^{-1}

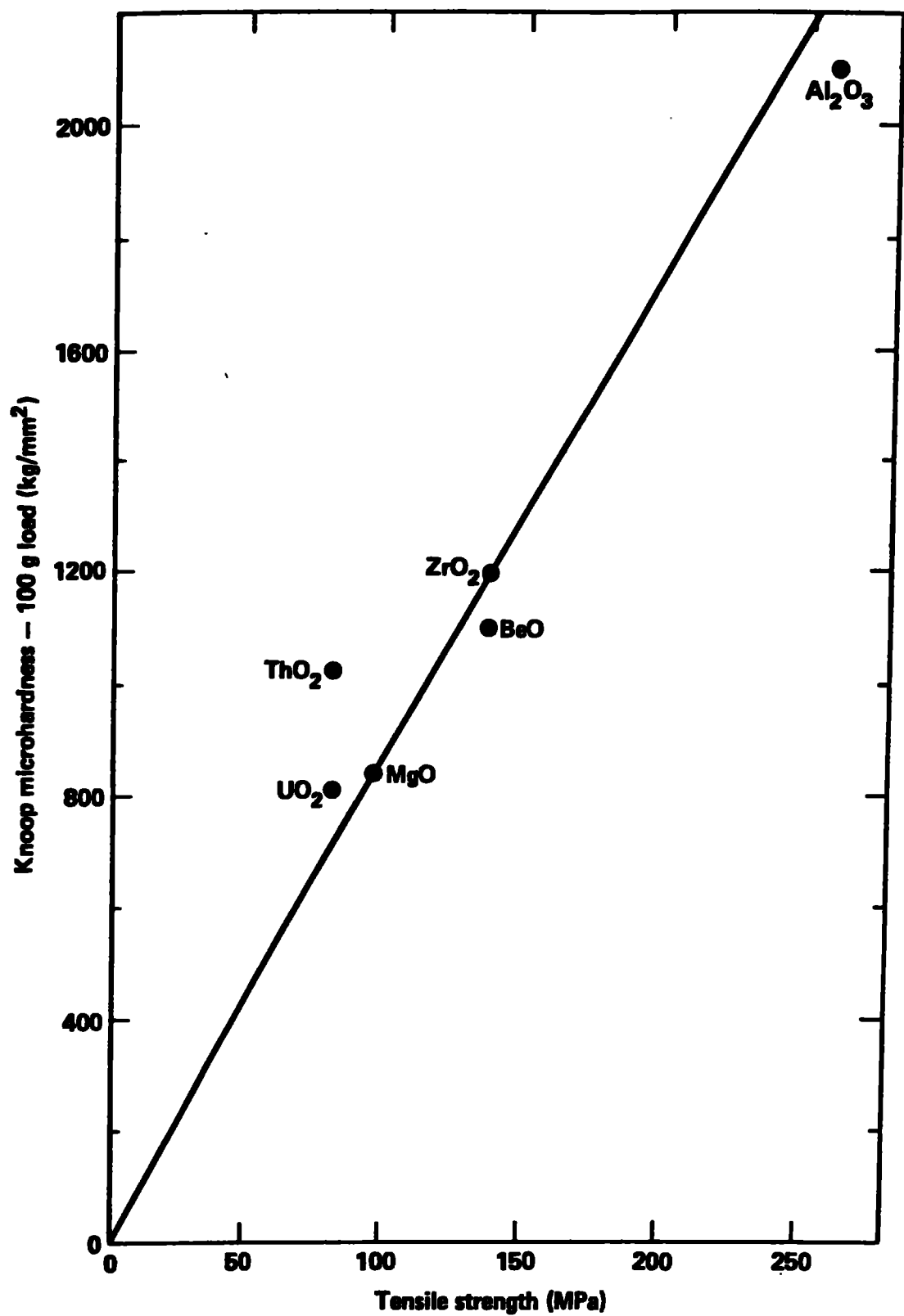


Figure 1

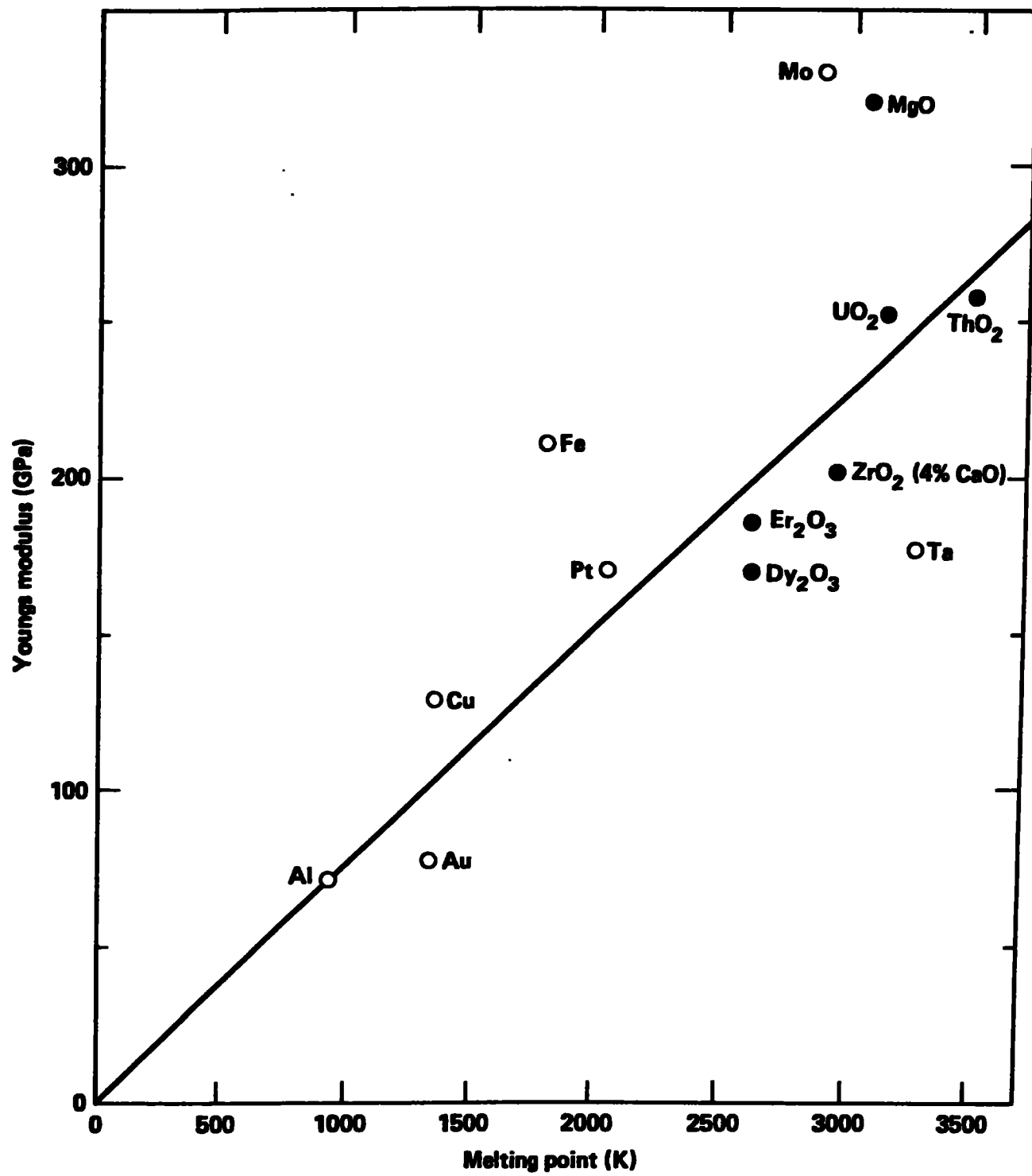


Figure 2

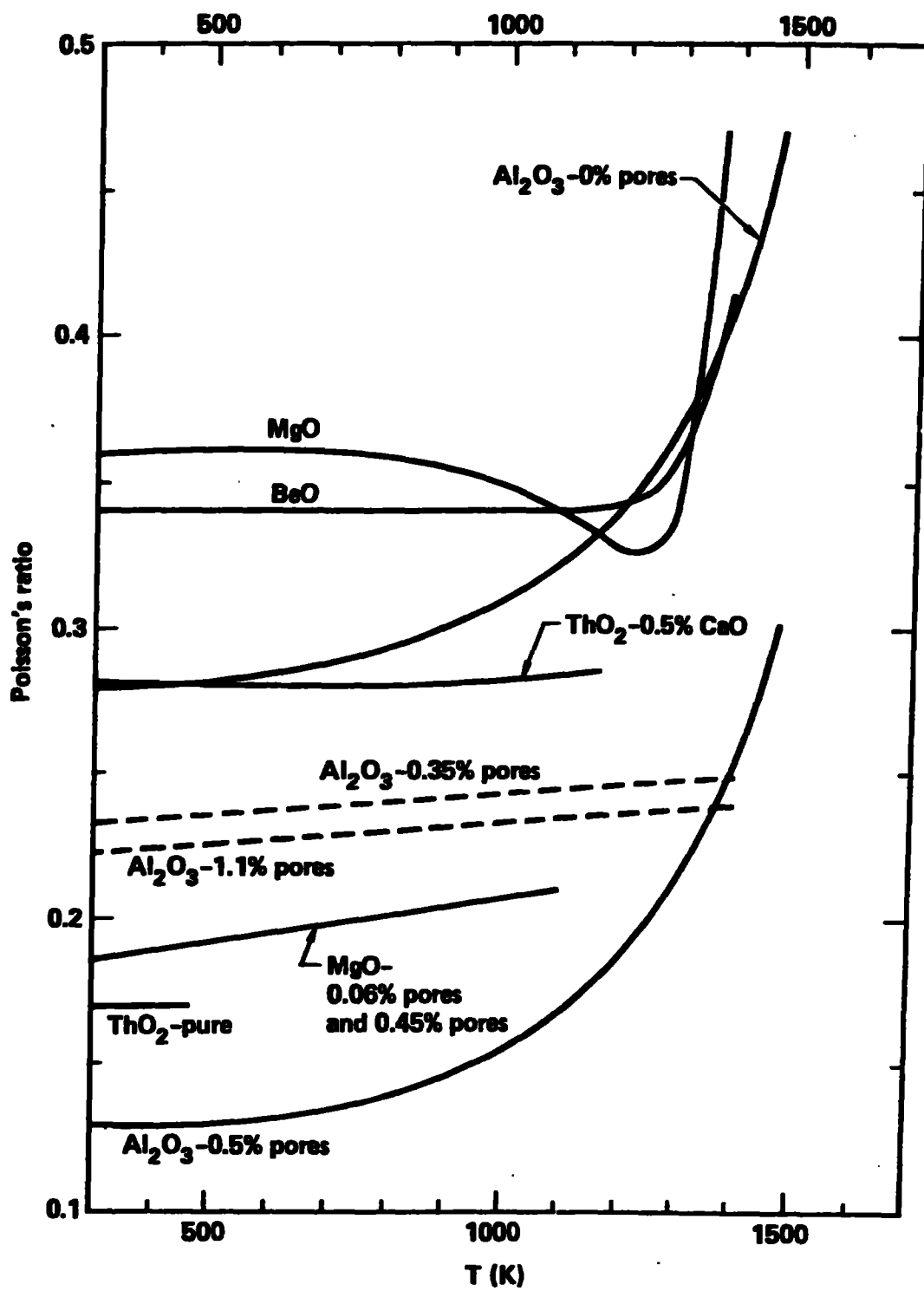


Figure 3

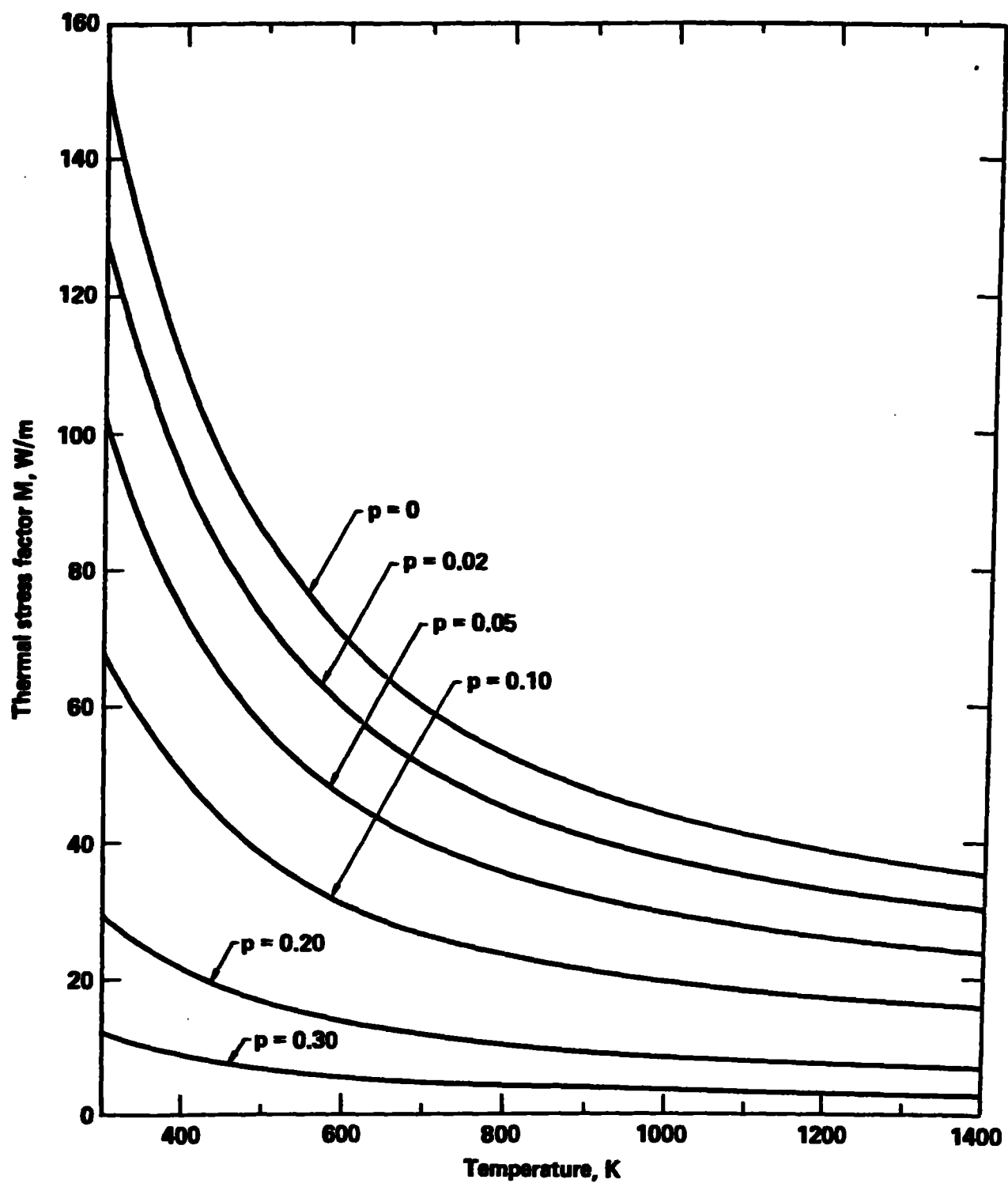


Figure 4

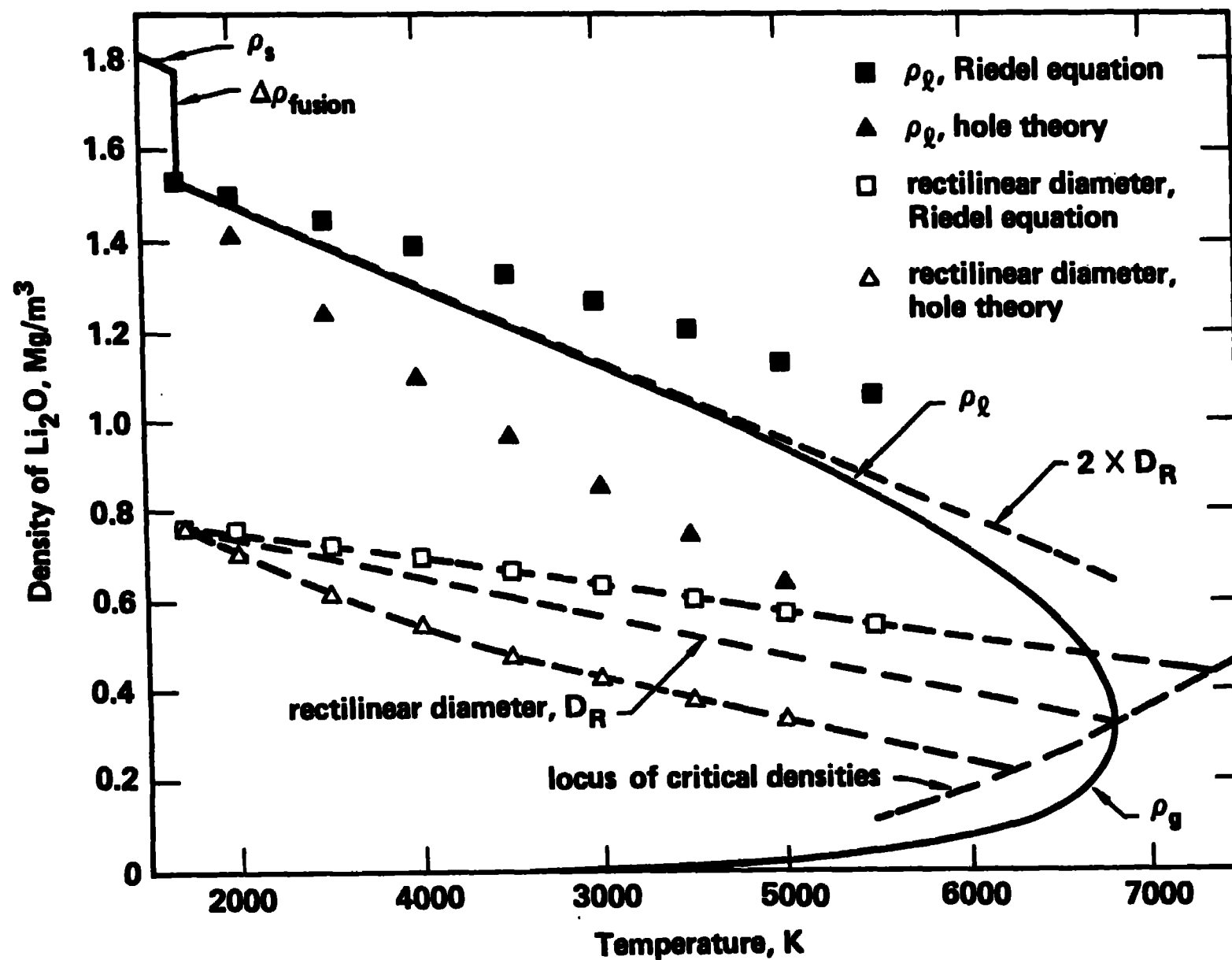


Figure 5